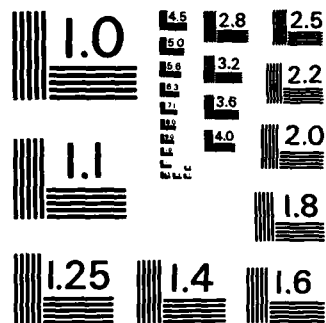END

FILMED

DTIC

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

AFWAL-TR-85-2011

DEMONSTRATION OF A PYROELECTRIC CONVERSION POWER
CYCLE WITH A POLYMER

RANDALL B. OLSEN

CHRONOS RESEARCH LABORATORIES, INC.   **AD-A158 964**
3025 VIA DE CABALLO
OLIVENHAIN, CALIFORNIA 92024

MARCH 1985

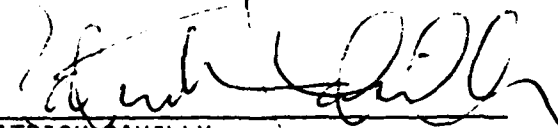FINAL REPORT FOR PERIOD OCTOBER 1983 - OCTOBER 1984

DTIC FILE COPY

85 09 09 008

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

W. PATRICK RAHILLY
Project Engineer
Power Components Branch
Aerospace Power Division
Aero Propulsion Laboratory
FOR THE COMMANDER

PAUL R. BERTHEAUD
Chief, Power Components Branch
Aerospace Power Division
Aero Propulsion Laboratory

JAMES D. REAMS
Chief, Aerospace Power Division
Aero Propulsion Laboratory

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/POOC, *W-PAFB, OH 45433 to help us maintain a current mailing list".*

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AD-A158 964

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
	Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
	AFWAL-TR-85-2011

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Chronos Research Laboratories, Inc.		AFWAL/POOC

6c. ADDRESS (City, State and ZIP Code)	7b. ADDRESS (City, State and ZIP Code)
3025 Via De Caballo, Olivenhain, CA 92024	Wright-Patterson AFB, OH 45433

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
	AFWAL/POOC	F33615-83-C-2344

8c. ADDRESS (City, State and ZIP Code)	10. SOURCE OF FUNDING NOS.			
Wright-Patterson AFB, OH 45433	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
	61102F	2308	S8	04

11. TITLE (Include Security Classification) Demonstration of a Pyroelectric Conversion Power Cycle with a Polymer

12. PERSONAL AUTHOR(S) Randall B. Olsen

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
Final	FROM Oct 83 TO Oct 84	1985 March	63

16. SUPPLEMENTARY NOTATION

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	ENERGY CONVERSION
1001	2202	2012	PYROELECTRIC
			POLYMERS

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Copolymers of vinylidene fluoride trifluoroethylene P(VDF-TrFE) exhibit large piezoelectric effects. Standard isothermal D-E hysteresis loops were found to be inaccurate predictors of the pyroelectric conversion performance of this material. Conduction effects obscured the observation of conversion cycles for the presently available materials. A conversion cycle was measured with electric energy density of 30 mJ/cm^3, which is 15 times larger than that of any other polymer yet measured. Resistivity and displacement change data are discussed in terms of predicted pyroelectric energy conversion performance.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL
James F. Holt	(513) 255 6235	AFWAL/POOC

DD FORM 1473, 83 APR   EDITION OF 1 JAN 73 IS OBSOLETE.

PREFACE

For further information contact:

W.P. Rahilly
AFWAL/POOC-2
Bldg. 18   Rm A201
Wright-Patterson AFB,
Ohio 45433
(513) 255-6235

R.B. Olsen
Chronos Research Laboratories,
Inc.
3025 Via De Caballo
Olivenhain, CA 92024
(619) 756-1447

iii

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

SECTION I

INTRODUCTION

The pyroelectric effect is the flow of charge to and from
the surfaces of a material resulting from a change in
temperature.[1] This effect may be used for the conversion of heat
directly into electrical energy. In spite of its apparent lack of
promise in the early 1960s this approach to energy conversion has
been revived by recent advances. Some researchers are now
suggesting that this type of conversion may be more efficient
than previously believed.[2,3] In addition, in the past couple of
years, pyroelectric generators have been built which produce more
than four orders of magnitude greater power than the devices of
twenty years ago.[4,5,6]

A pyroelectric converter is a form of heat engine which
directly transforms heat energy into electrical energy. The
thermodynamics of the pyroelectric converter are analogous to the
more familiar steam engine with pressure-volume mechanical work
replaced by voltage-charge electrical output.

Shown in Fig. 1 is an overlay of the charge-voltage
(displacement versus electric field (D-E)) characteristics of a
pyroelectric (ferroelectric) material at two different
temperatures. A thermal- electrical cycle may be executed in
which an amount of electrical energy,

$$\oint Vdq = \text{Shaded area of Fig. 1}, \qquad (1)$$

may be produced. This cycle is an electrical analog of the
Ericsson heat engine cycle. Details of the cycle have been
presented previously.[7]

The data shown in Fig. 1 correspond to measurements on a ceramic of lead zirconate modified with tin and titanium (PZST). The discovery of this material, with its unusually good pyroelectric properties, allowed the recent upsurge in the development of pyroelectric conversion.[4,5,6]

Now, however, a potentially more attractive pyroelectric material is appearing. Several workers[8-12] have reported the first polymer, vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)), shown to have a clear-cut ferroelectric to paraelectric transition. Such a transition is necessary for highly active thermodynamic medium for use in pyroconversion. The homopolymer P(VDF) transition seems to be at or above its melting temperature apparently rendering it useless for such conversion.[13,14]

Recent attempts[15] to demonstrate the energy conversion cycle of Fig. 1 with P(VDF-TrFE) indicate that the reversible change in the displacement is smaller than was expected from the temperature dependence of D-E loops. Furthermore, conduction losses appeared to be important in the first conversion cycle experiments with P(VDF-TrFE). The present study was initiated to better quantify a) the reversible displacement changes induced by changing temperature and b) the resistivity of P(VDF-TrFE) at various temperatures.

SECTION II

EXPERIMENT--MATERIAL PROPERTIES

Resins of vinylidene fluoride - trifluoroethylene copolymer were supplied by Daikin Kogyo Co., Lt. The copolymer film samples were prepared by pressing the resin powder between two hot (195C), smooth, and flat nickel platens to form thin (30 to 70 micrometer) sheets. In early work the dielectric strength in the polymer of interest at 90C was roughly 600 kV/cm. Later in this investigation, extended duration (12 hours plus) vacuum (50 mTorr) bake-out of residual monomer and other impurities about 140C improved the dielectric strength. The films were not mechanically stretched to orient polymer chains. Aluminum electrodes 2.5 or 5.0 cm^2 of overlap area were evaporated onto the films. Electrical leads were attached by silver epoxy to the overhanging tabs of the aluminum electrodes. The specimen was held on a clean pyrex holder and placed in high dielectric grade silicon oil (Dow Corning DC 200) forced convection bath.

Both resistivity and displacement change of each specimen were measured with an uncompensated Sawyer-Tower circuit.[16] A relatively large (10 μF) capacitor was used to integrate the charge so as to minimize the error induced in the voltage measurement (due to the small voltage drop across this integrating capacitor).

The conduction current of each specimen was measured by applying a given voltage and then measuring the change in the amount of charge on the integrating capacitor (divided by time). No effort was made to systematically determine the time

dependence though it was observed that the conduction generally declined after several minutes. The main emphasis of the measurements was to determine both the magnitude and temperature dependence of the resistivity of P(VDF-TrFE).

The electric field dependence of the reversible electric displacement change due to thermal cycling between room temperature and 90C was also determined. The measurement which was performed was fundamentally similar to standard pyroelectric measurements, but with some important differences. Standard pyroelectric measurements are performed at (or near) zero electric field so as to avoid conduction currents. Very sensitive measurements of displacement (polarization) change can be performed at zero field and A.C. techniques can be used with very small thermal oscillations.[17] Under high field conditions, conduction effects become very large and small temperature fluctuation methods become impractical. For the purpose of the present study it was necessary to devise a method of changing the temperature of a specimen very rapidly. Normal convection oil baths require several tens of minutes to warm up and perhaps hours to cool down. A method for cycling temperatures in about 10 seconds has been described recently.[15] For this study, however, even faster temperature changes were required. Higher speed thermal cycling was achieved with a dual convection oil bath system. The specimen was attached to a pyrex holder and placed in the cool (room temperature) bath. A given voltage was applied and after about two minutes the specimen was rapidly transferred into the hot oil bath. After an additional 5 to 10 seconds the specimen was returned to the original bath. The high

4

voltage was maintained on the specimen throughout the "dunking" procedure. The "dunking" was repeated several times before the displacement change was measured.

Before each series of dunk tests the specimen was cycled at room temperatures and its D-E hysteresis loop was observed. At the conclusion of each dunk series the specimen was once again electrically cycled at room temperature to determine that no changes had occurred during the series. Occasional dielectric breakdown took place in several samples, but the corresponding data have been excluded from this report. Furthermore, no changes in room temperature D-E hysteresis loops were observed in any specimen discussed here.

SECTION III

RESULTS--MATERIAL PROPERTIES

Figure 2 illustrates the resistivity of 73/27 P(VDF-TrFE) as a function of temperature in the range from 20C to 90C. Measurements were made with electric fields ranging from 0.2 to 1.0 MV/cm. The resistance was measured for time periods from 20 seconds to 50 minutes. The spread in the measurements at each temperature is partially due to non-ohmic conduction, i.e. higher electric fields result in lower resistivities at each temperature. The spread in the data is also due to time dependent conduction processes. The lower resistance points for each temperature in Fig. 2 correspond to measurements taken early (from 20 to 200 seconds) after applying the voltage, while the higher resistance points correspond to measurements taken several tens of minutes after the voltage had been applied. This time dependent spread in resistance values is not surprising in light of the time dependence measurements of Munick[18] on a variety of other polymers. Munick showed that for low electric fields (~2kV/cm), resistivity increased by roughly a factor of ten for each decade in time in the time range between 10 and 10,000 seconds. Part of the spread in the data is also suspected to be due to slow polarization processes.

In spite of the difficulties inherent in these measurements, it is possible to draw an approximate trend line to indicate the temperature dependence of the resistivity. The resistivity falls by a factor of 100 as the temperature is increased from 20C to 100C.

SECTION VII

EXPERIMENT--POWER CONVERSION CYCLE

Resins of vinylidene fluoride - trifluoroethylene copolymer were supplied by Daikin Kogyo Co., Lt. The copolymer film samples were prepared by pressing the resin powder between two hot (190C), smooth, and flat nickel platens to form thin (30 to 70 micrometer) sheets. In early work the dielectric strength in the polymer of interest at 90C was roughly 600 kV/cm. Later in this investigation, extended duration (12 hours plus) vacuum (50 mTorr) bake-out of residual monomer and other impurities at 140C improved both the dielectric strength and the resistivity. The films were not mechanically stretched to orient polymer chains. Aluminum electrodes 2.5 or 5.0 cm^2 of overlap area were evaporated onto the films. Electrical leads were attached by silver epoxy to the overhanging tabs of the aluminum electrodes.

The experimental measurement involves the thermodynamic cycling of the pyroelectric copolymer. The type of cycle which was described in Section VI requires that a specimen of pyroelectric polymer be subjected to both thermal and electrical oscillations. The experimental apparatus (a similar device has been described previously[5]) which performs the simultaneous variation of these two parameters therefore consists of two major systems. One system controls the electrical behavior of the test polymer, the other system manages the heat flow. Consider first the system which imposes the necessary temperature oscillations on the specimen.

the electric field and the spontaneous polarization, the higher dielectric strength of the copolymer represents a very important improvement. The present dielectric strength of commercial capacitor grade homopolymer P(VDF) is yet another five times greater (5 MV/cm). It is expected that the copolymer dielectric strength may, with proper processing, achieve comparable strength.

It is helpful to estimate the electrical output energy density which is possible using this new copolymer material. Since electrical output energy density is equal to the product of displacement density times electric field (corresponding to the area in Figure 10) the scale of this density is, (for the copolymer), 25 Joule/cm^3 (5 μC/cm^2 X 5 MV/cm). Actual cycles do not utilize the complete energy density calculated this way and are smaller by a factor of three or four. Thus it is estimated that P(VDF-TrFE) may produce an impressive 7 J/cm^3 per cycle once its dielectric strength is improved to that of capacitor grade P(VDF). This would represent a 35 fold improvement in energy density as compared with the ceramic (PZST).

$$\oint Vdq = \text{Shaded area of Figure 10,} \qquad (2)$$

may be produced. This cycle is an electrical analog of the

Ericsson heat engine cycle.

The spontaneous polarization is of key importance because it

sets the scale for the amount of displacement change which is

achievable in a conversion cycle. Along with the dielectric

strength, the remanent polarization determines the order of

magnitude of the amount of electric work which may be produced in

a thermodynamic cycle.

The data shown in Figures 9 and 10 correspond to measurements

on a ceramic of lead zirconate modified with tin and titanium

(PZST). The discovery of this material, with its unusually good

pyroelectric properties, allowed the recent upsurge in the

development of pyroelectric conversion.[4,5,6]

Now, however, an even more attractive pyroelectric material

is appearing. Japanese workers[8-12] have reported the first

polymer, P(VDF-TrFE), shown to have an observable ferroelectric

to paraelectric transition. Such a transition is necessary for a

highly active thermodynamic medium for use in pyroconversion.

Thermodynamically, the copolymer is impressive. P(VDF-TrFE)

has a transition similar to that shown for the ceramic PZST in

Figure 9 with a few important differences. One difference is that

the transition (ferroelectric to paraelectric) occurs at a lower

temperature. Much more importantly though, the dielectric

strength of the copolymer is presently twenty five times greater

than that of the ceramic. Since the electrical output energy

density of the pyroelectric converter scales as the product of

18

For any cyclic process an area on a charge-voltage diagram represents an electrical work since

$$W = \oint Vdq \qquad (1)$$

where W=electrical work, V=voltage, and q=charge. The direction of the path (clockwise or counterclockwise) determines whether electrical energy is produced or dissipated. A familiar example is the hysteretic heating of a ferroelectric element. Every time that the voltage applied to a ferroelectric sample is cycled isothermally, an amount of electrical energy (equal to the hysteresis loop area) is dissipated as heat. In this case the loop is cycled in the counterclockwise sense, as indicated by the arrows in Figure 9.

The pyroelectric generator exploits the fact that, by removing the isothermal constraint, it is possible to reverse the direction in which the loop is cycled. The loop may be cycled in a clockwise sense, thus resulting in the production of electrical energy from heat.

Shown in Figure 10 is an overlay of the charge-voltage characteristics of a ferroelectric at two different temperatures. Figure 10 also shows how clockwise cycling may be achieved when operating between these two temperatures. Starting in the upper right-hand corner at high voltage and low temperature, the FE is discharged as it is heated. After reaching a high temperature, the FE is further discharged by reducing the externally applied voltage. Thus, an electrical cycle may be executed in a clockwise manner -- opposite to the hysteretic loop direction -- in which an amount of electrical energy,

17

SECTION VI

PYROELECTRIC POWER CONVERSION CYCLE

A pyroelectric converter is a form of heat engine which
directly transforms heat energy into electrical energy. The
thermodynamics of the pyroelectric converter are analogous to the
more familiar steam engine with pressure-volume mechanical work
replaced by voltage-charge electrical output. In addition to
operating as a generator of electrical energy from heat, a
pyroelectric converter may be "run backwards" to provide either
heat pumping or refrigeration. In refrigeration, the
electrocaloric effect, which is analogous to the widely known
magnetocaloric effect, can operate in a manner similar to
adiabatic demagnetization cooling. Before describing the
proposed pyroelectric conversion experiments an introduction to
the basic thermodynamic cycle (from the electrical energy
producing point of view) will be helpful.

The electrical energy production cycle may be described in
terms of the charge-voltage behavior of a ferroelectric material
(FE). Figure 9 illustrates, at various temperatures, the charge-
voltage (displacement versus applied electric field) behavior of
a ferroelectric material which may be utilized for pyroelectric
conversion. Notice that the displacement is not a single valued
function of the applied electric field. The displacement depends
in a hysteretic way upon the applied field. The remanent
displacement (which is the focus of this investigation) is the
amount of displacement which remains when the externally applied
voltage is reduced to zero.

16

SECTION V

APPLYING THE COPOLYMER TO POWER CONVERSION

Early experiments on pyroelectric conversion for space applications by Beam, Fry and Russel[27,28] were not encouraging primarily because of the particular choice of thermal-electrical cycle and the lack of a pyroelectric material with high performance characteristics. In a theoretical study done in 1965 Margosian[29] summarized:

"With currently known materials, this generator is

too heavy to be of interest for electric propulsion.

As a source of auxiliary power it is comparable, at

best, to solar cells in weight. If materials with

substantially better characteristics than those

considered are found, competitive performance as a

power source might be possible."

The copolymer of the present study, vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) is expected to fulfill that promise. Section VI describes the pyroelectric conversion cycle. Subsequent sections detail measurements on the first observation of such cycles P(VDF-TrFE).

problems. Significantly higher energy density pyroelectric conversion should be possible with more highly resistive P(VDF-TrFE) which will allow thermal cycling to above the ferroelectric to paraelectric transition temperature.

As materials with higher resistivities (and presumably greater resistance to irreversible polarization decay) become available, greater details about the high field transition behavior of P(VDF-TrFE) will be forthcoming.

elsewhere.   The room temperature (zero electric field) pyroelectric coefficient, P_3, for 52/48 P(VDF-TrFE) is in the range of -3 to -5 $nC/cm^2 K$ and for 73/27 P(VDF-TrFE) it is about -2 to -3 $nC/cm^2 K$.   A pyroelectric coefficient times a temperature amplitude yields a number which can be compared with the present electric displacement change measurements.   For the case of 52/48 P(VDF-TrFE), 20 K times $-P_3$ gives 0.06 to 0.10 uC/cm^2.   The data of Fig. 7 shows the displacement change of about 0.1 uC/cm^2 at elevated temperatures (40 to 60C) and moderate fields and between 0.15 and 0.25 uC/cm^2 at high field.   In the case of 73/27 P(VDF-TrFE), 65 K times $-P_3$ gives 0.13 to 0.20 uC/cm^2.   The data of Fig. 6 shows the displacement change of 0.10 to 0.15 uC/cm^2 at elevated temperatures and high electric fields.   Thus, for the range of temperatures and fields investigated here, the displacement changes are well approximated by the (zero field) room temperature pyroelectric coefficients.

A comment on predicted pyroelectric energy conversion performance is in order.   If the high field pyroelectric properties of the material of this study where used in a pyroelectric energy converter, the performance of the converter would be moderate.   The energy density (assuming no hysteresis or conduction losses) would be about 0.2 uC/cm^2 times 0.5 MV/cm or 0.1 J/cm^3-cycle.   This energy density would be about half that of lead zirconate titanate[7], which has been used in pyroelectric conversion demonstration devices.[4,5]   The value of 0.1 J/cm^3 - cycle is, however, greater than that which has been shown in actual conversion cycle measurements with the copolymer[15] (0.03 J/cm^3 -cycle) which have suffered from electric conduction

field) for 52/48 P(VDF-TrFE) occurs at about 65C.[24]   It was

therefore anticipated that rather large changes in displacement

would have been observed if this composition had been cycled from

20C to 90C. Unfortunately, the range of observability in the

present experiment was limited to 60C and below due to conduction

effects.   The changes for 52/48 P(VDF-TrFE) were about twice as

large as those seen in 73/27 P(VDF-TrFE) even with the restricted

cycling range of 40 to 60C.   At higher temperatures, displacement

changes perhaps as large as $1 \mu C/cm^2$ or greater might be

expected.   However, the ferroelectric state may be expected to be

field induced at temperatures substantially above the zero field

Curie transition temperature.   Such a shift due to electric field

is well established for more traditional ferroelectric materials

(crystals and ceramics) and is required by thermodynamics.[1,25]

More highly resistive materials are required in order to observe

polarization changes at such elevated temperatures with the

present experimental technique.

The copolymer 37/63 P(VDF-TrFE) displayed displacement

changes about twice as large as those of 73/27 P(VDF-TrFE for

similar thermal cycles (23 to 90C).   Although DSC measurements

have shown no ferroelectric to paraelectric transition,[12,24]

dielectric measurements[12] suggest a Curie transition at ~60C.

Hysteresis loops show considerable change between 40C and 70C.[15]

With this in mind, the relatively large displacement changes

observed with the 37/63 composition are not unexpected.

The size of the displacement changes measured here may be

compared with pyroelectric coefficient measurements reported

12

SECTION IV

DISCUSSION--MATERIAL PROPERTIES

Figures 2, and 3 illustrate that the resistivity of P(VDF-TrFE) may range from 10^{12} to 10^{16} ohm-cm depending on the composition, temperature (in the range 20-100C), electric field and the amount of time the field is applied. At elevated temperatures (increased conductivity), it has been shown[22,23] that quasi-irreversible changes in the amount of polarization can take place. Under the restricted conditions of the present measurement (temperature less than or equal to 90C and no bipolar field cycling at high temperature) quasi-irreversible displacement reductions were not detected.

Displacement change measurements performed at high electric field must contend with large conduction signals. But the conduction effects can, with an acceptable error be subtracted. The displacement change data shows a mild increase in magnitude as the molar content of TrFE is increased. Such behavior might have been anticipated in light of the known decrease in the ferroelectric - paraelectric transition temperature with increasing TrFE content. Since the thermal cycling temperature range, 20-90C, is below the Curie point (roughly 120C, for 73/27 P(VDF-TrFE)[22,24] at zero field) large changes in displacement were neither anticipated nor seen for this composition. The highest pyroelectric conversion performance occurs near the ferroelectric to paraelectric transition temperature (see for example Ref. 7). Differential scanning calorimetry (DSC) peaks indicate that the ferroelectric - paraelectric transition (zero

11

to differing conduction corrections. The fields accessible in these measurements were limited by conduction. The general increase in the size of the reversible displacement changes with electric field probably reflects a restricted repoling ability at low fields. The coercive field for the copolymers, 400kV/cm, corresponds to the field at which the displacement change becomes large in Fig. 7. Fig. 8 shows the displacement changes for 37/63 P(VDF-TrFE). Changes as large as $0.3 \mu C/cm2$ were observed. Again, repoling problems are suspected to be causing the reduced changes at low field.

Fig. 4. It is apparent that the measurement A should be larger than B and C should be larger than D due to differences in the conduction current subtraction. In cases where the conduction currents tends to be very small (negligible slope in regions 1,3 and 5 of Fig. 4) the measurements A,B,C and D are expected to converge on a single value.

Fig. 5 shows actual data corresponding to a dunk displacement change measurement. Fig. 5 closely resembles Fig. 4 except that an extra feature is seen. In region 3 (Fig. 5) the slope is not constant. The slope increases after time T_2 because as the specimen is pulled out of the hot oil bath it begins to cool slowly in the air and the repoling process actually starts before time T_3 when the cooling dunk into the room temperature bath occurs.

Fig. 6 summarizes the electric field dependent reversible displacement changes for the dunk measurements performed between room temperature and 90C for 73/27 P(VDF-TrFE). The displacement changes for the high resistivity 73/27 are tightly grouped and are nearly independent of field up to 900 kV/cm. The small value of displacement change, 0.1 to 0.15 μC/cm2 results from the fact that the temperature change, 25 to 90C, is well below the ferroelectric to paraelectric transition temperature.[22]

The displacement changes of 52/48 P(VDF-TrFE) are shown in Fig. 7. In spite of a smaller thermal cycle amplitude (40C to 60C), the changes are about twice as large as those seen in 73/27 P(VDF-TrFE). The relatively greater spread among the different measurements, A, B, C and D, reflects the expected divergence due

9

composition). An energy term was not deduced for 37/63 P(VDF-TrFE) due to the large spread in the data.

An ideal polarization change measurement is depicted in Fig. 4. The relative charge is plotted versus time. At early times, region 1, the specimen is held at room temperature. The finite slope in region 1 indicates the small amount of conduction current flow through the specimen. At time T_1, the specimen is quickly dunked into the hot convection oil bath. The most immediate effect is that the specimen rapidly depoles partially, i.e. the displacement decreases. Some "roundedness" to the displacement change after dunking is expected due to the finite rate of heat transfer, and because of slow polarization effects. After the displacement change has occurred the specimen is at high temperature, thus the conduction current increases and so does the slope in region 3 of Fig. 4. At time T_2 the specimen is pulled out of the hot bath and at time T_3 it is dunked into the cooler ambient temperature bath. This time the specimen repoles (displacement increases) and then, in region 5, the slope levels off once more to a value corresponding to room temperature conduction.

Estimates of the displacement are taken at four places along the curve. The relative charge change measured at A in Fig. 4 is the difference between the charge just before time T_1 and a back extrapolation of the high temperature conduction line from region 3 as shown. The relative charge change B is the difference between a forward extrapolation of region 1 and the value at the beginning of region 3. Changes C and D are similarly defined in

8

The temperature dependence of the resistivity may be interpreted with the ionic conduction equation

$$J = J_o \, \exp\left[-(W/2e_s + U)/KT\right] \times \sinh(eaE/KT) \qquad (2)$$

where J is the current density, J_o is a constant, W is the energy required to separate ions in a medium of unit dielectric constant, e_s is the dielectric constant, U is the potential energy barrier height for ion traps located an apparent jump distance "a" apart, E is the electric field strength, e is the charge of an electron, and K is Boltzmann's constant.[19] If the hyperbolic sine term is ignored[20,21], the slope on an Arrhenius plot of (minus) log(resistivity) against 1/T gives the energy term $(W/2e_s + U)$. The energy term for the 73/27 P(VDF-TrFE) data of Fig. 2 is 1.4 eV

Measurements on other batches of the copolymer have shown that the resistivity can be quite variable. Fig. 3 is similar to Fig. 2, but it displays the resistivity data for 52/48 P(VDF-TrFE). The batch of 52/48 copolymer exhibited resistivities of about 5×10^{14} and about 10^{12} ohm-cm at temperatures of 20C and 90C respectively. Compared with the resistivity displayed in Fig. 2 for the composition 73/27, the 52/48 material is about 20 times more conductive at 20C and nearly 200 times more conductive at 90C. An Arrhenius plot of the data of Fig. 3 indicates that the energy term, $(W/2e_s + U)$, is 2.2 eV.

Resistivity versus temperature of another composition, 37/63 P(VDF-TrFE), was also measured. Its resistivity was roughly 10^{13} ohm-cm at 90C (i.e. 20 times more conductive than the 73/27

7

A schematic view of the experimental apparatus is shown in Figure 11. The key element of the experiment is the spiral stack in which the copolymer specimen is placed. As shown from the top in Figure 12, the spiral is wound around a central support rod. The spiral consists of alternate layers of plastic sheet and nylon separator screen. Wrapped into the spiral stack is the copolymer specimen. The nylon separator screen allows heat exchange fluid (a high dielectric strength silicone oil) to flow over the surface of the plastic sheet and the specimen. The heat exchange fluid is pumped by a piston which is in the cylinder below the stack. A temperature gradient is imposed upon the fluid by the heater which resides in the top of the stack and the cooler (heat exchanger) which sits below the stack. Since the fluid is hotter in its top portion and cooler in its lower portion, the net result of pumping the fluid up and down through the stack is that the specimen temperature is forced to oscillate.

The piston position is changed by a stepping motor. The stepping motor is physically linked to the piston via a pinon and rack gear, and the stepping motor is controlled by a microprocessor. The maximum displacement of the piston is approximately 10 cm which corresponds to 4000 steps of the stepping motor. The pumping cycle period is typically in the range of 2 to 10 seconds.

The input heat to the apparatus comes from an electrical heater in the form of a stainless steel band which is wound into the spiral stack. The heater power (1300 watt maximum) is

controlled by sensing the temperature in the heater with a thermocouple, feeding the information to a digital controller, and then switching on and off the heater current with a solid state relay. Heat is extracted from the apparatus by heat exchanger which is cooled by tap water. Control of the cooling power of the heat exchanger is analogous to control of the heater. In the cooling heat exchanger case, however, the opening and closing of a solenoid valve on the cooling water line is used to control the temperature of the cooler. The maximum temperature which may be produced at the specimen is about 90C with the present design.

The electrical system contains two primary components. One system controls the voltage of the copolymer specimen. It also coordinates the timing of voltage changes with the thermal conditions of the specimen. Meanwhile the other electrical system measures the pyroelectric cycle of the specimen. The electrical measurement system will be described first.

The charge-voltage behavior of the pyroelectric conversion cycle of the specimen is measured with an uncompensated Sawyer-Tower circuit.[14,16,30] A relatively large (19.6 μF) capacitor is used to integrate the charge so as to minimize the error induced in the voltage measurement (due to the small voltage drop across this integrating capacitor). Simultaneous readings of both charge and voltage of the specimen are recorded on a storage oscilloscope.

To achieve the electrical analog of an Ericsson cycle, certain control and coordination of the thermal and electrical oscillations must be obtained. To produce the Ericsson

22

thermodynamic cycle, it is necessary to change the applied
voltage on the specimen whenever the specimen's temperature
reaches either a maximum or a minimum. At low pumping frequency,
the extremal temperatures occur at the high and low points of the
fluid pumping stroke. Therefore, the coordination between
temperature and applied voltage may be accomplished by assuring
that voltage ramp-ups and voltage ramp-downs occur at the ends of
the fluid pumping stroke. The computer receives signals from the
pump's stepping motor microprocessor so that it knows when to
send out a command to change the voltage on the specimen. The
computer controls the output of a 10 kilovolt bipolar power
supply via a digital to analog converter.

Once the specimen is in place and all of the thermal and
electrical cycling conditions have been provided, the actual
measurement is straightforward. The experiment consists of the
measuring the charge - voltage behavior of the specimen as a
function of thermal and electrical cycling limits.

SECTION VIII

RESULTS--POWER CONVERSION CYCLE

Before beginning the power cycle experiments a number of
standard isothermal hysteresis curves were measured at 2 Hz.
Figure 13 is representative of the earliest of such measurements
on P(VDF-TrFE) which is 73% VDF. Several curves were measured on
specimens held within the thermal cycling apparatus under
isothermal conditions achieved by stopping the fluid pumping
piston during the measurement of the hysteresis cycle. The
hysteresis cycles so measured were essentially identical to other
hysteresis cycles which were measured in a standard isothermal
oil bath arrangement.[12] The cycles in Figure 13 were made on
materials for which bake-out procedures had not been performed.

Figure 14 shows the room temperature hysteresis loop for a
specimen which had been processed with the careful bake-out
procedure. The dielectric strength was increased to about 1
MV/cm. An important secondary effect of the increase in the
electric field limit is that the electric displacement was also
increased.

In spite of the resistivity increase which was achieved by
the bake-out procedure, the measured "power cycles" were
extremely distorted from the ideal (expected) cycles by
conduction.

It is helpful to review what was expected in these cycle
measurements. The expected displacement change (implied by
Figure 13) was about 1.5 μC/cm^2. Furthermore this displacement

24

change was anticipated to be much greater than the amount of charge conducted through the copolymer specimen during the cycling period. The charge per unit area conducted through the copolymer, q_c, is given by

$$q_c = \int_0^T J(E,T)\ dt \sim J(E_{max},T_{max})\ T = E_{max}\ T\ /\ \rho(E_{max},T_{max}) \qquad (4)$$

where J is the conduction current per unit area, rho is the bulk electrical resistivity, and both J and ρ are functions of electric field E and temperature T. The conduction charge was expected to be about $0.12\ \mu C/cm^2$ (assuming $\rho = 10^{13}$ ohm-cm, $E=4\times10^5$ V/cm , $T=3s$). Thus the displacement charge was expected to be about ten times larger than the conduction charge.

As it turns out, the temperature dependence indicated by Figure 13 may be dominated by quasi-irreversible changes similar to those reported recently by Davis et al.[22] and Olsen et al.[23] The quasi-irreversible behavior stems from the appreciable conductivity at elevated temperatures which in the presence of electric fields leads to greatly reduced displacement. The phenomenon is described as quasi-irreversible because as Davis et. al reported after heating the copolymer above the ferroelectric to paraelectric transition temperature, the room temperature hysteresis (displacement) can be restored.

Therefore the reversible component of the temperature dependence of the displacement change is likely to be over estimated by the data of Figure 13. Preliminary measurements of the reversible component[31] indicate that it is about $0.15\ \mu C/cm^2$ (i.e. a factor of ten smaller than suggested by Figure 13).

25

Figure 14 shows the improved isothermal hysteresis loop which results from 140C annealing.

In addition to the smaller than expected displacement changes, the resistivity was observed to be less than 10^{13} ohm-cm in most specimens at the temperatures of interest for pyroelectric cycling. A detailed study of both the high field resistivity and of the reversible displacement changes will be presented elsewhere.[31]

To summarize then, the highly distorted power cycles resulted from displacement changes (ten times smaller than expected) which were obscured by conduction.

In spite of the problems which were encountered, it was possible to measure modest pyroelectric power cycles as shown in Figure 15. The cycle of Figure 15 still suffers from a substantial amount of drift which is due to conduction of charge though the bulk of the copolymer specimen. The points 1 through 7 indicate consecutive times in the cycle. In the vertical line 2-3, the conduction process adds to the apparent displacement change. By contrast, in the vertical line 4-5, conduction diminishes the apparent displacement change. The conducted charge at high electric field is larger than it is at low field. For all fields the effect of conduction is to make the cycles drift upward in both Figure 15. The size of the reversible displacement was at least $0.1 \mu C/cm^2$ according to the high field line 4-5 and less than $0.18 \mu C/cm^2$ according to the low field line 2-3. This is in agreement with displacement change measurements taken at fixed field.[31] The electrical output energy density demonstrated by Figure 15 is about 30 milliJoule per cubic centimeter per cycle.

26

This output is about an order or magnitude smaller than that demonstrated for the ceramic material PZST.[7]

SECTION IX

DISCUSSION--POWER CONVERSION CYCLE

Previous to the present study, three main relationships between standard isothermal hysteresis loops and pyroelectric energy conversion cycles appeared to be valid. The relationships were, 1) the temperature dependence of isothermal loops could be used to estimate the pyroelectric cycle behavior, 2) the hysteretic loss of the pyroconversion cycle would be overestimated by the hysteresis loops, and 3) the minimum field required for repoling in the pyroelectric cycle would be overestimated by the hysteresis loops.

For previous pyroelectric materials, it has generally been found that the temperature dependence of standard isothermal hysteresis loops could be used as a reasonable predictor of pyroelectric cycle behavior. It has been shown previously[7] that isothermal loops of PZST yield good estimates of the pyroelectric cycle performance of that material. In the present study it was found that the presence of a quasi-irreversible displacement change can give rise to hysteresis loops whose temperature dependence is much larger (by a factor of ten) than the displacement changes which occur in the corresponding pyroelectric conversion cycles.

Bipolar (standard) hysteresis loops usually overestimate the hysteresis loss associated with a pyroconversion cycle, but the error in the ceramic PZST case was not great. For PZST, bipolar hysteresis loops estimate the loss as being 20% whereas the unipolar hysteresis loops (see reference 7) indicate that the

28

loss is only 10% as large as the output energy density. In the

present study, the hysteresis loops of Figure 13 appear to

indicate that hysteresis may entirely consume the pyroelectric

conversion cycle. In other words, there is almost no "gap"

between the hysteresis loops at two different temperatures in

Figure 13. The "gap" between the two hysteresis loops in Figure

10 seems to form the region in which the pyroelectric cycle can

be performed. As it turns out, pyroelectric cycles can be

performed in spite of a lack of gap in the bipolar loops. The

hysteresis loops of the copolymers exhibit very high coercive

fields which overlap the gap region which would otherwise be

apparent if unipolar loops were used in a manner as described

previously.[7] Thus copolymer hysteresis loops appear to indicate

that pyroconversion cycles will be wiped out by hysteretic

processes. However pyroelectric conversion cycles are possible.

The bipolar hysteresis loop simply over-predicts the amount of

hysteresis associated with the pyroelectric cycle. In the

previous ceramic the over-prediction was small. In the present

copolymer case over-prediction leads to a totally false

implication.

The third relationship between hysteresis loops and

pyroconversion cycles is that the low field (cooling) repoling

portion of the cycles is overpredicted by the hysteresis loops.

In the ceramic PZST case, the coercive field is very small (about

one tenth as large as the dielectric strength) and the resulting

error of the prediction is small.[7] However in the copolymer

case, the coercive field is about half as large as the breakdown

strength of the material. Hence the error in the copolymer case

may be very large. Related measurements on displacement changes indicate that significant repoling[31] occurs at fields as low as 100 kV/cm. Thus hysteresis loops may be of limited utility as indicators of the minimum repoling field for copolymer pyroconversion cycles.

A pair of comments on the relatively small size of the observed pyroelectric conversion cycle are in order. The cycle which was measured was far from what could be considered an optimal cycle for the copolymer. Of the copolymer ratios studied only one (73/27) was resistive enough to permit observation of the cycle. Unfortunately the 73/27 material could be studied only in a temperature range substantially below its Curie point (which according to DSC measurements[22] is at about 130C while heating). It is now well established that the largest pyroelectric conversion cycles are obtained near and above the Curie point of a given material. It is therefore expected that much larger cycles will be obtained with the copolymer once resins are available with increased resistivity (about 10^{15} ohm-cm) above their Curie temperatures.

Though the energy density of the present study is considered to be small for the copolymer, its magnitude still represents a very substantial increase over any previously measured polymer. The largest known measurement of any other polymer was that of Beam et al.[28] in which about 2 mJ/cm^3 were measured in a different type of cycle of tetrafluoroethylene - hexafluoropropylene. Therefore the present measurement represents a 15-fold increase in the energy density observed with

30

a polymer.

Future efforts on pyroelectric energy conversion materials should continue to stress maximizing the electrical output energy density while also requiring high resistivity.

REFERENCES

1. M. E. Lines and A. M. Glass, <u>Principles</u> <u>and</u> <u>Applications</u> <u>of</u> <u>Ferroelectrics</u> <u>and</u> <u>Related</u> <u>Materials</u>, Clarendon, Oxford (1977).

2. J. E. Drummond, "Dielectric power conversion," 10th IECEC, p. 569, (1975).

3. J. A. Gonzalo, "Ferroelectric materials as energy converters," Ferroelectrics <u>11</u>, 423 (1976).

4. R. B. Olsen, "Ferroelectric conversion of heat to electrical energy--a demonstration," J. Energy, March/April (1982).

5. R. B. Olsen, J. M. Briscoe, D. A. Bruno, and W. F. Butler, "A pyroelectric energy converter which employs regeneration," Ferroelectrics <u>38</u>, 975 (1981).

6. R. B. Olsen, J. M. Briscoe, and D. A. Bruno, "Performance of a 1-watt pyroelectric converter," 17th IECEC (1982).

7. R. B. Olsen and D. Evans, J. Appl. Phys., <u>54</u> 5941 (1983).

8. T. Furukawa, M. Date, E. Fukada, Y. Tajitsu, and A. Chiba, "Ferroelectric behavior in the copolymer of vinylidene fluoride and trifluoroethylene," Jap. J. Appl. Phys. <u>19</u> (1980).

9. T. Furukawa, G. E. Johnson, H. E. Bair, Y. Tajitsu, A. Chiba, and E. Fukada, "Ferroelectric phase transition in a copolymer of vinylidene fluoride and trifluoroethylene," Ferroelectrics <u>32</u>, 61 (1981).

10. Y. Higashihata, J. Sako, and T. Yagi, "Piezoelectricity of vinylidene fluoride-trifluoroethylene copolymers," Ferroelectrics, <u>32</u>, 85 (1981).

11. T. Yamaka, T. Ueda, and T. Kitayama, "Ferroelectric-to-paraelectric phase transition of vinylidene fluoride-trifluoroethylene copolymer," J. Appl. Phys. <u>52</u>, 2 (1981).

32

12. T. Yamada and T. Kitayama, "Ferroelectric properties of vinylidene fluoride-trifluoroethylene copolymers," J. Appl. Phys. $\underline{52}$, 6863 (1981).

13. A. J. Lovenger, Macromolecules $\underline{16}$, 1529 (1983).

14. R. B. Olsen, J. C. Hicks, M.G. Broadhurst, and G. T. Davis, Temperature Dependent Ferroelectric Hysteresis Study of Poly(vinylidene fluoride) App. Phys. Let., $\underline{43}$, 127 (1983).

15. R.B. Olsen, D.A. Bruno, J.M. Briscoe, and E.W. Jacobs, J. Appl. Phys. [in press (May 1, 1985)]

16. C. B. Sawyer and C. H. Tower, Phys. Rev. $\underline{35}$, 269-273 (1930).

17. A.G. Chynoweth, J. Appl. Phys. $\underline{27}$, 27 (1956).

18. R.J. Munick, J. Appl. Phys. $\underline{27}$, 1114 (1956).

19. N.F. Mott, and R.W. Gurney, Electronic Processes in Ionic Crystals (Oxford U.P., Oxford, England, 1940), p. 40.

20. The relative change in the argument of the hyperbolic sine term due to temperature change is small (.02) compared with the change in the argument due to electric field change (1.0). Thus the temperature dependence of the hyperbolic sine term is masked by the variation arising from changes in the electric field.

21. M. Kosaki, K. Sugiyama, and M. Ieda, J. Appl. Phys. $\underline{42}$, 3388 (1971).

22. G. T. Davis, M. G. Broadhurst, Lovenger, and Furukawa, Ferroelectrics $\underline{57}$, 73 (1984).

23. R. B. Olsen, D. A. Bruno, J. M. Briscoe, and E. W. Jacobs, submitted to Ferroelectrics Letters.

24. T. Yagi, M. Tatemoto, and J. Sako, Polymer J. $\underline{12}$, 209 (1980).

25. D. Berlincourt, H. H. A. Kruegar, and B. Jaffee, J. Phys. Chem Solids 25, 659 (1963).

26. T. Furukawa, J. X. Wen, K. Suzuki, Y. Takashina, and M. Date, J. Appl. Phys. 56, 829 (1984).

27. B. H. Beam, "An exploratory study of thermoelectrostatic power generation for space flight applications," NASA TN-D336 (1960).

28. B. H. Beam, J. Fry, and L. Russel, "Experiments on radiant energy conversion using thin dielectric films," Progress in Astronautics and Aeronautics, Vol. 16, Space Power Systems Engineering, Editors: G. Szego and J. Taylor, Academic Press, 1964.

29. P. M. Margosian, "Parametric study of a thermoelectrostatic generator for space applications," Lewis Research Center, NASA, Cleveland, Ohio, Jan. 4, 1965.

30. J. C. Hicks, T. E. Jones, M. L. Burgener, and R. B. Olsen, "High temperature hysteresis in polyvinylidene fluoride," Ferroelectrics Letters, 44, 89-92 (1982).

31. R. B. Olsen, D. A. Bruno, J. M. Briscoe, and E. W. Jacobs, submitted to J. Appl. Phys.
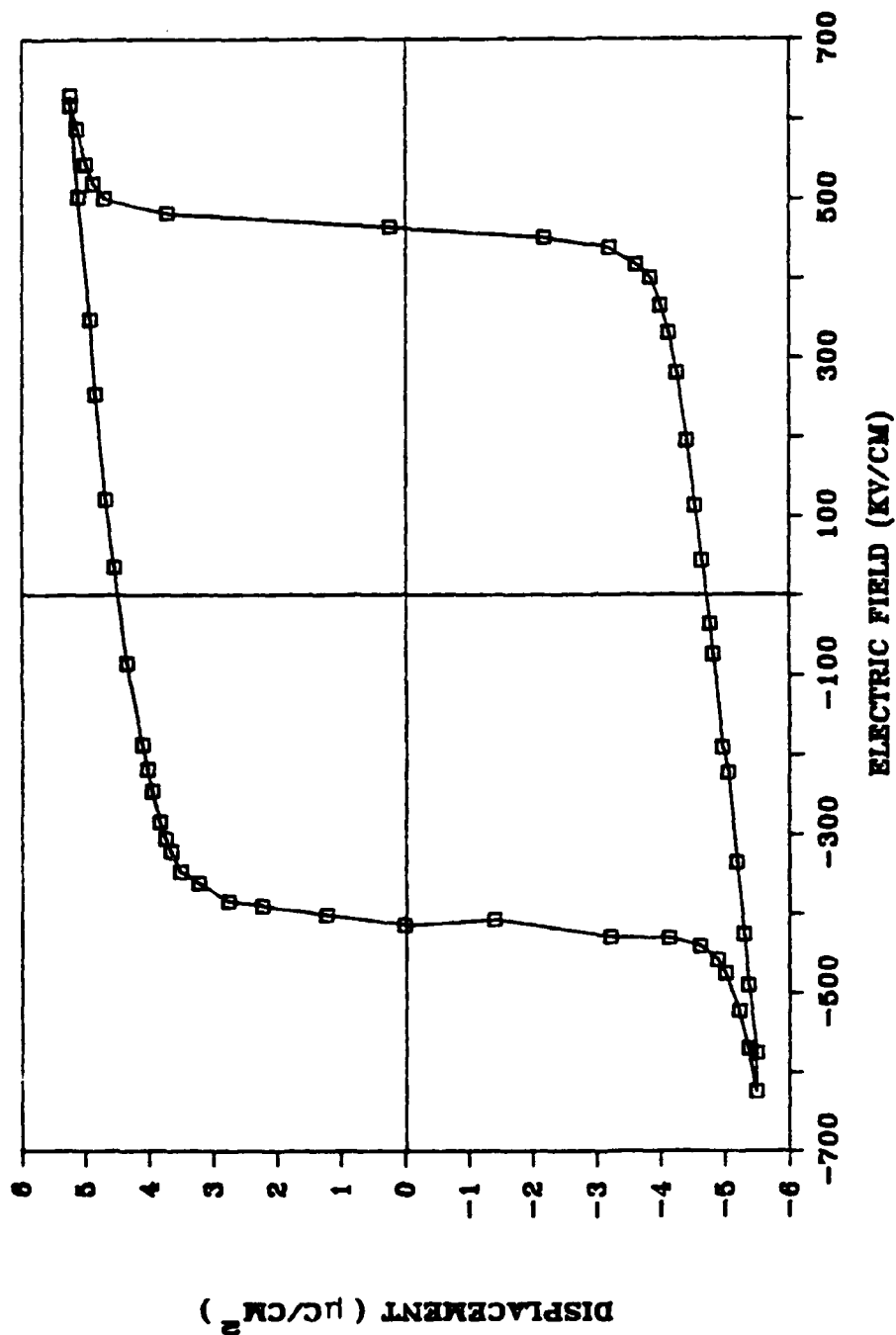
FIG. 14. Displacement vs. electric field (D-E) hysteresis loop
for P(VDF-TrFE), which is 73% VDF, at 27C. This
specimen had been processed with the bake-out procedure
described in the text.
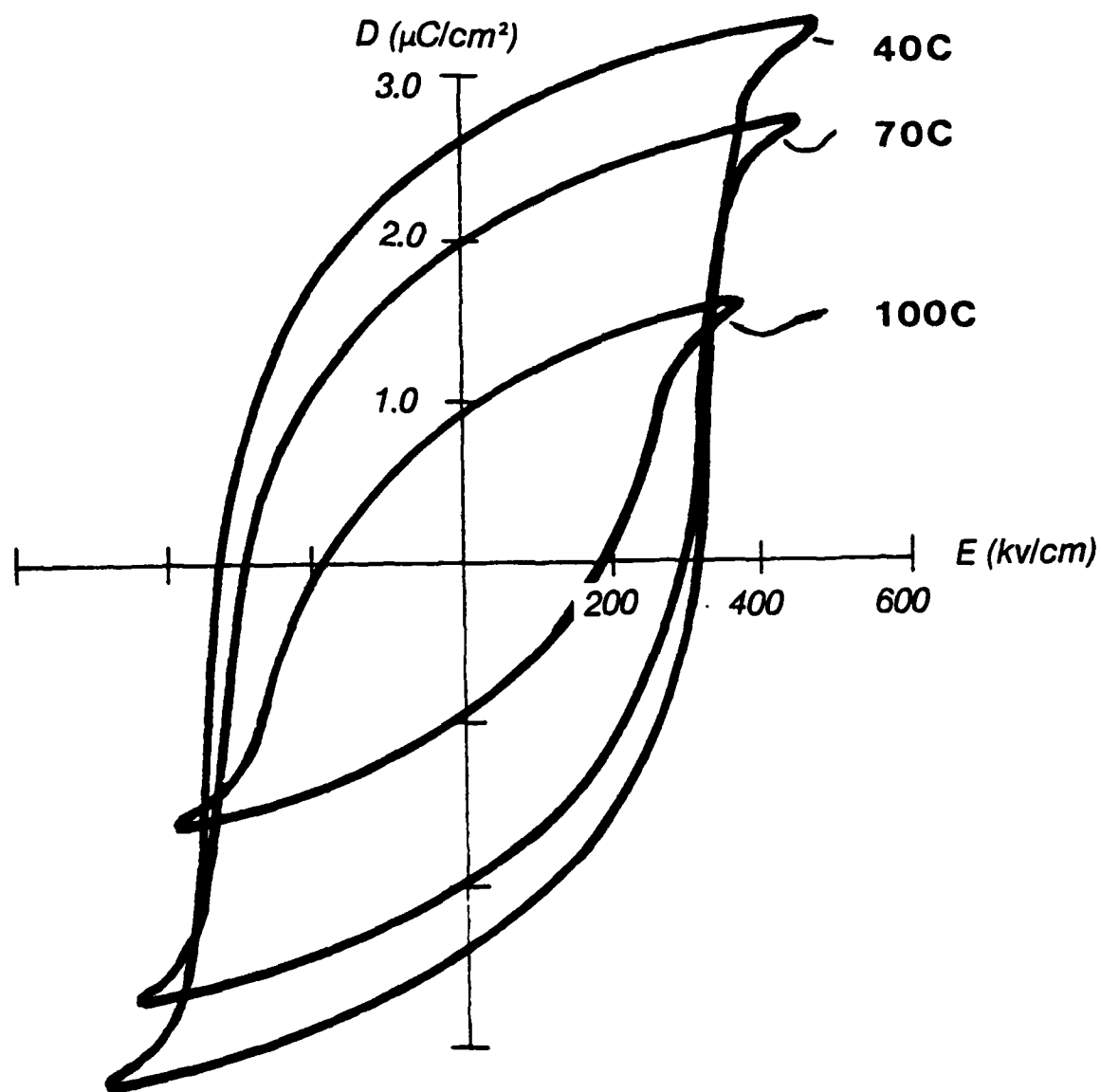
FIG. 13. Displacement vs. electric field (D-E) hysteresis loops for P(VDF-TrFE), which is 73% VDF, at 40C, 70C and 100C.
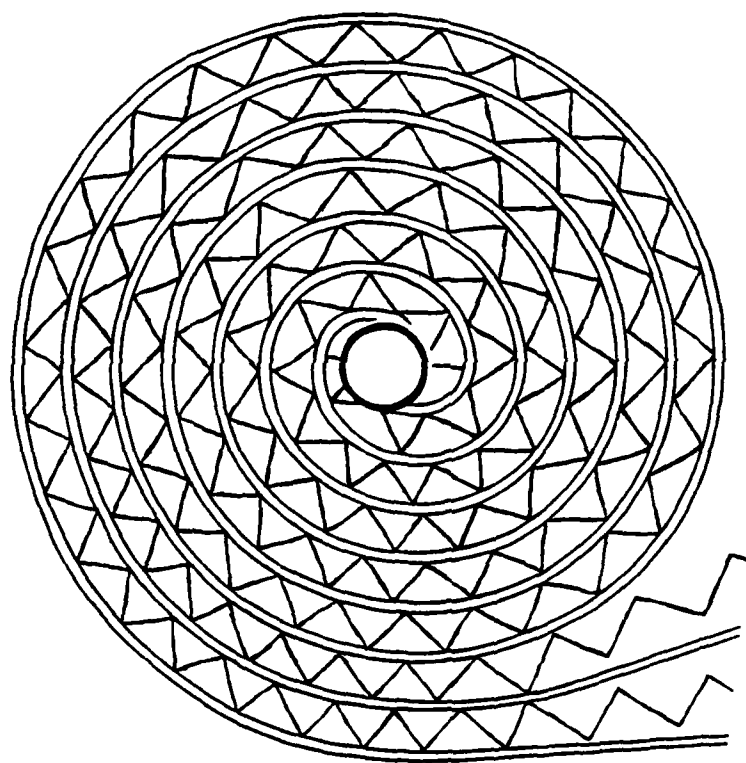
FIG. 12. Top view of the stack shown in FIG.11. The spiral consists of alternate layers of plastic sheet and nylon separator screen. The copolymer specimen is wrapped into the stack.
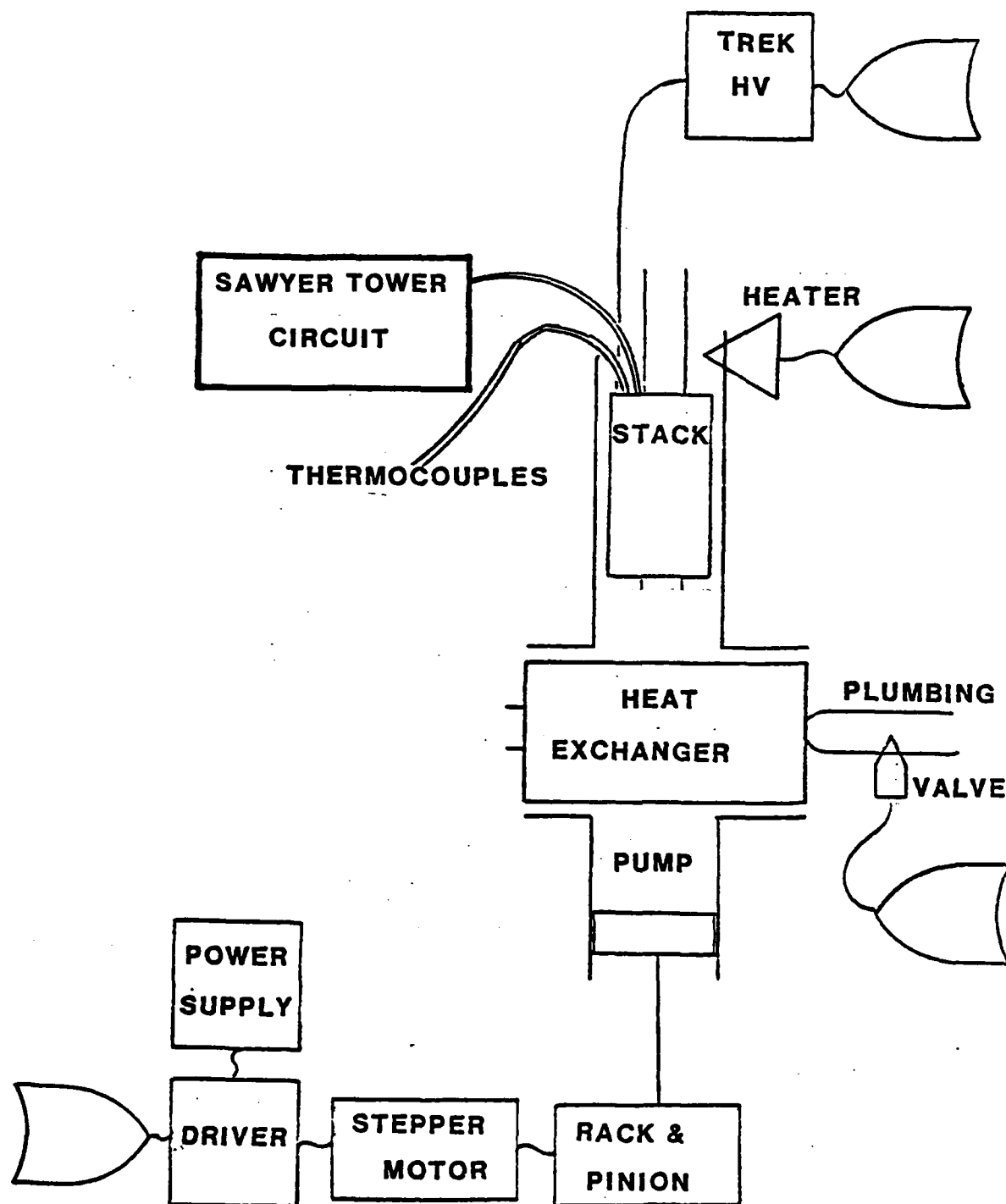
FIG. 11. Schematic of experimental apparatus in which
temperature and electric field of pyroelectric
conversion materials are cycled.
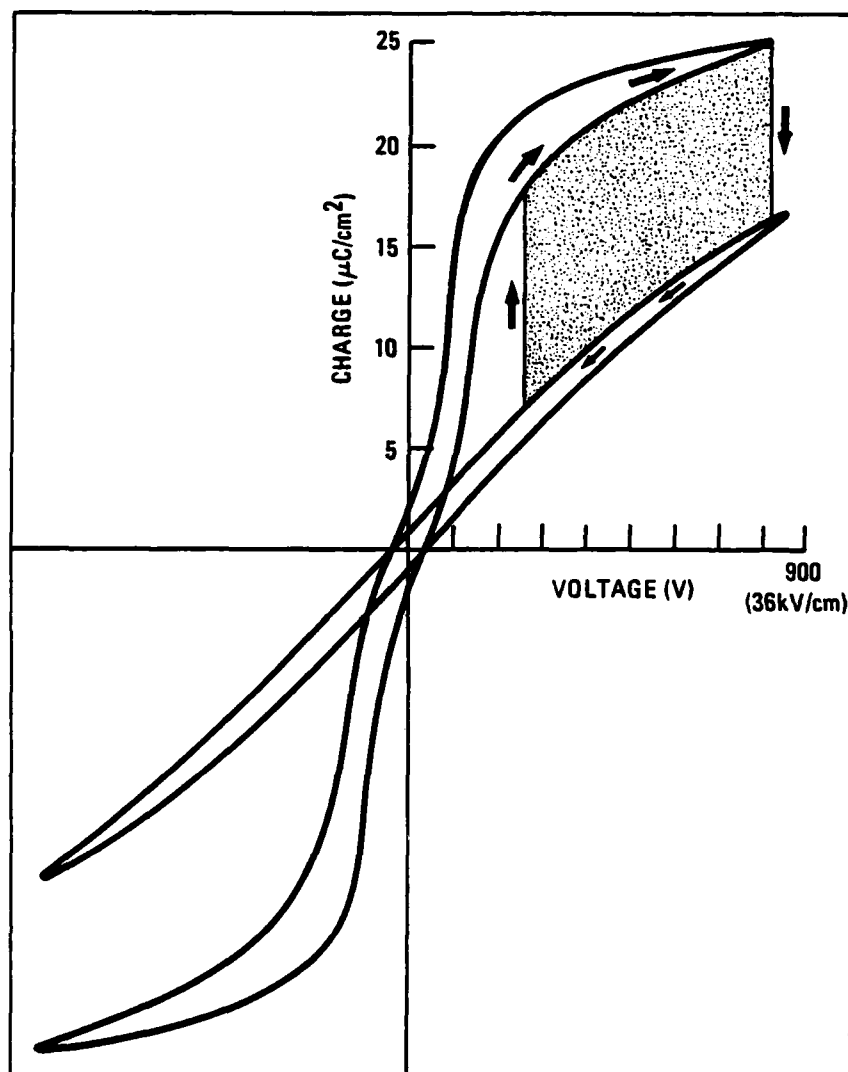
FIG. 10. Electrical energy production cycle may be realized by appropriately phased changes in temperature and applied electric field. The shaded area is equal to the electrical energy per cycle which may be produced by Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.68}$,Sn$_{0.25}$,Ti$_{0.07}$)$_{0.98}$O$_3$.

44

FIG. 9.   Charge (displacement) vs. applied voltage (electric
           field) for various temperatures of 0.025-cm-thick
           Pb   Nb   (Zr   ,Sn   ,Ti   )   O .
             0.99 0.02   0.68   0.25   0.07 0.98 3

43
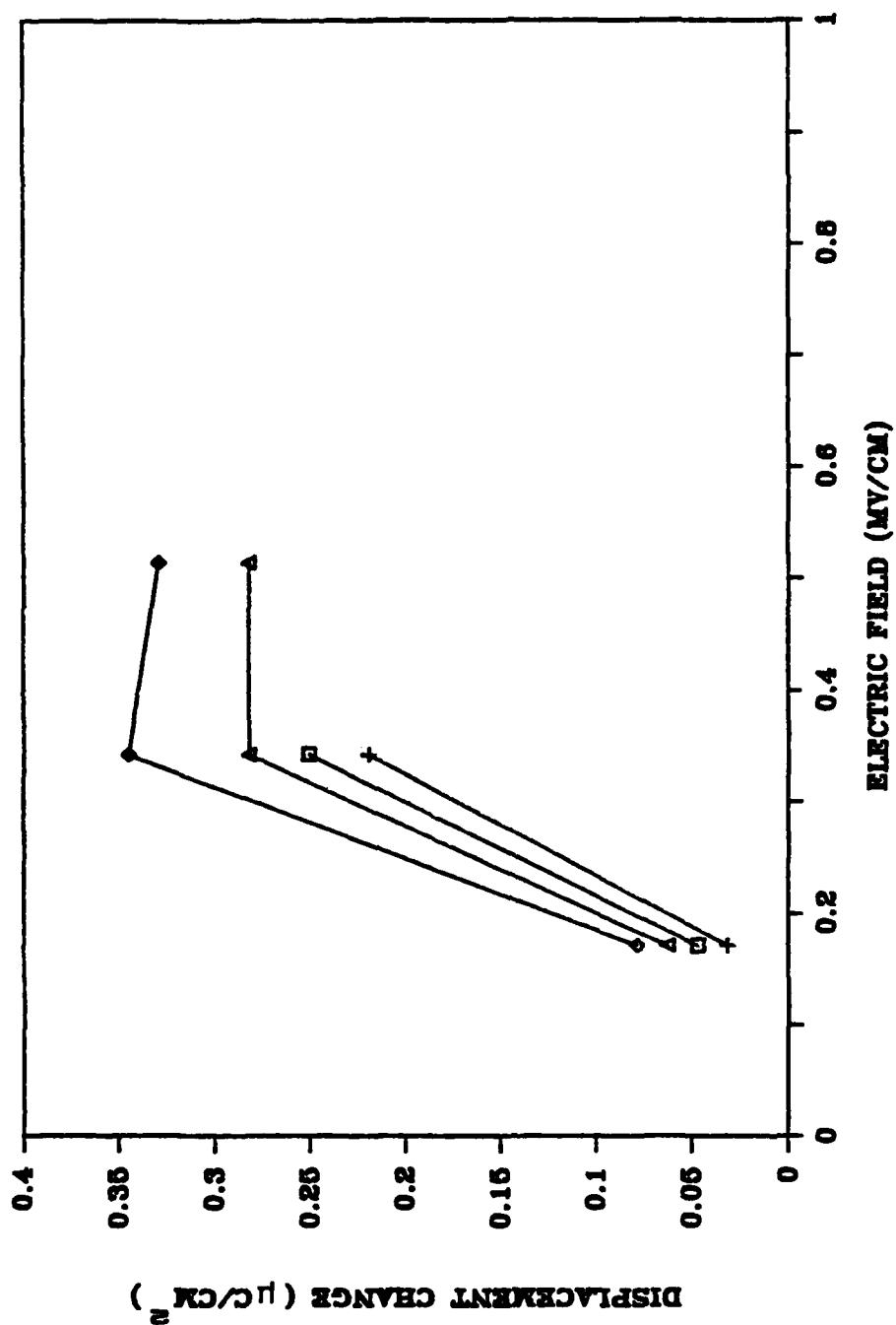
FIG. 8. Displacement change vs. electric field for 37/63 P(VDF-TrFE) for thermal cycling between 23 and 90C. The various estimates, □ A, + B, ◇ C, and ◄ D, of the displacement change are defined in Fig. 4.
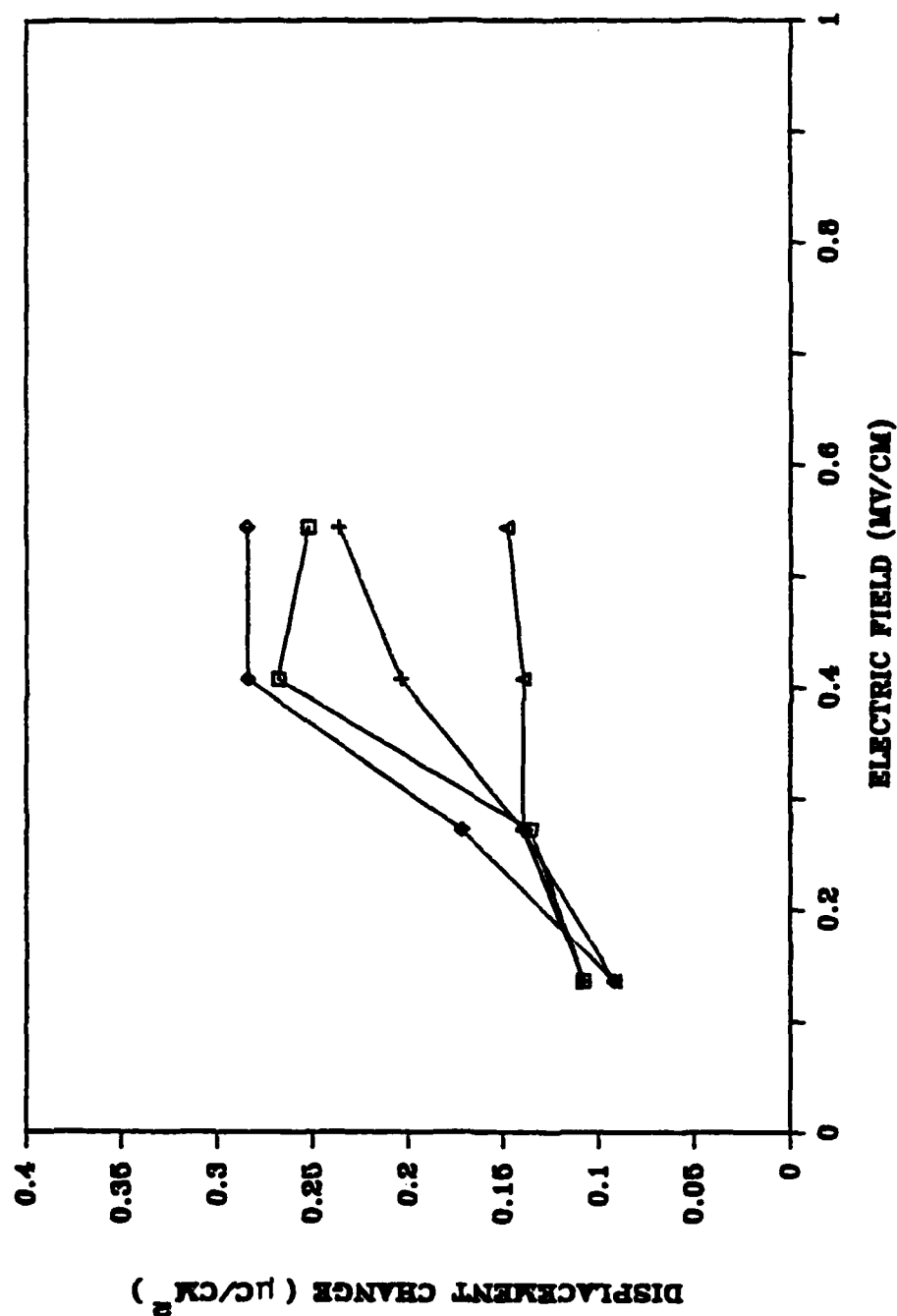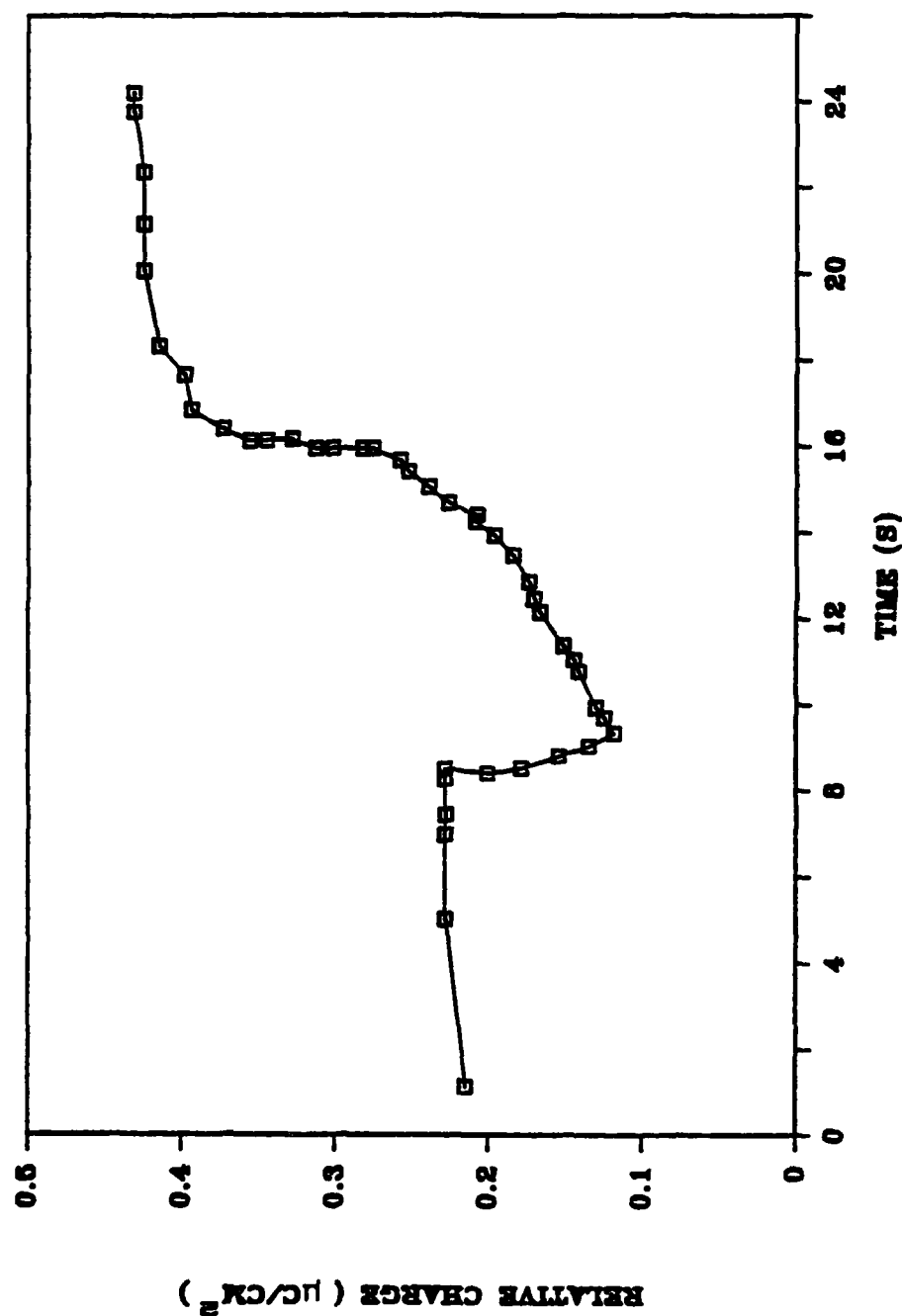
FIG. 7. Displacement change vs. electric field for 52/48 P(VDF-TrFE) for thermal cycling between 40 and 60C. The various estimates, □ A, ╋ B, ◇ C, and ▲ D, of the displacement change are defined in Fig. 4.
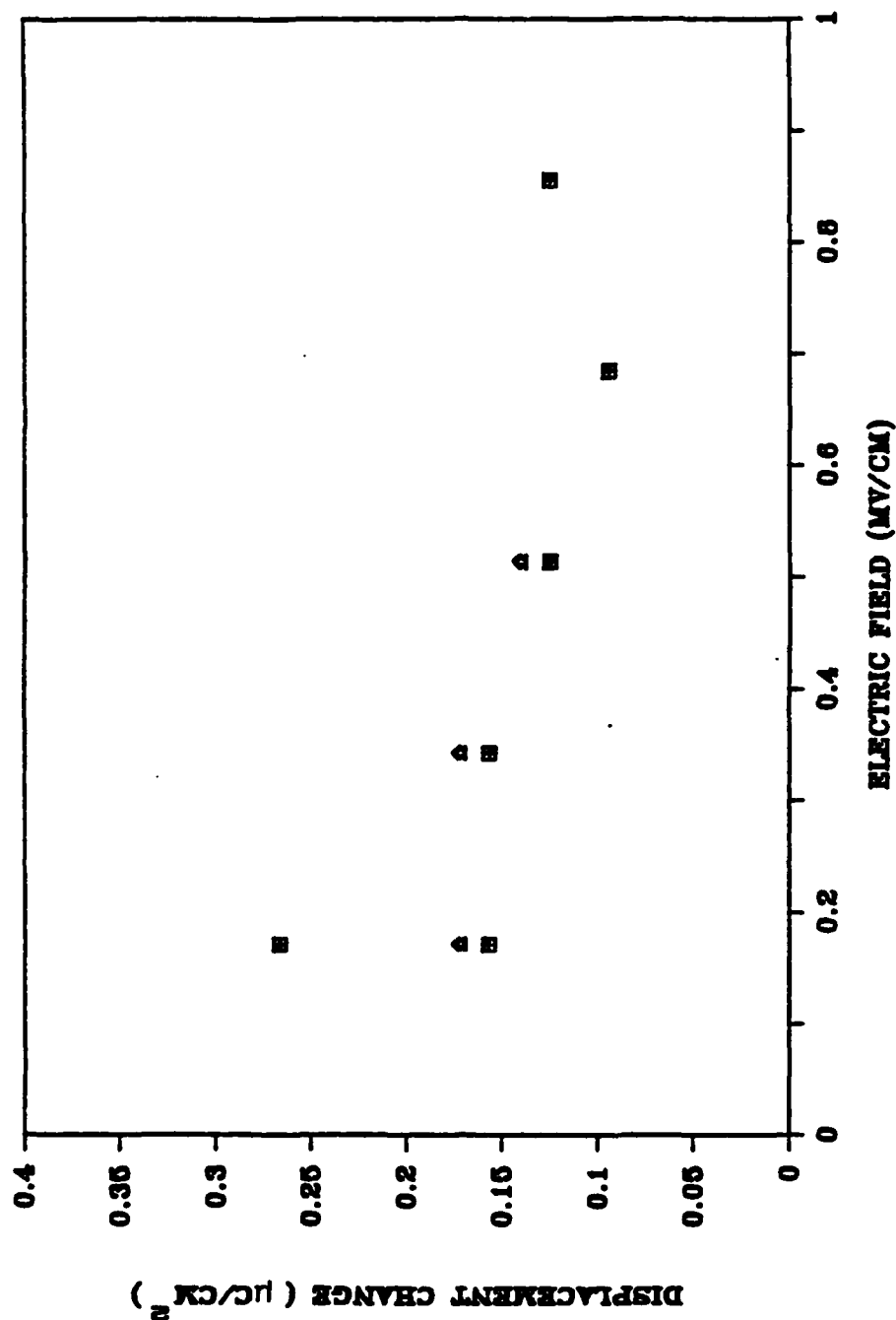
FIG. 6. Displacement change vs. electric field for 73/27 P(VDF-TrFE) for thermal cycling between 25 and 90C. The various estimates, ☐ A, ✛ B, ◇ C, and ◆ D, of the displacement change are defined in Fig. 4.

FIG. 5. Typical data of relative charge versus time for "dunk" displacement change measurements. The material is 73/27 P(VDF-TrFE) measured at about 300 kV/cm between 25 and 90C.
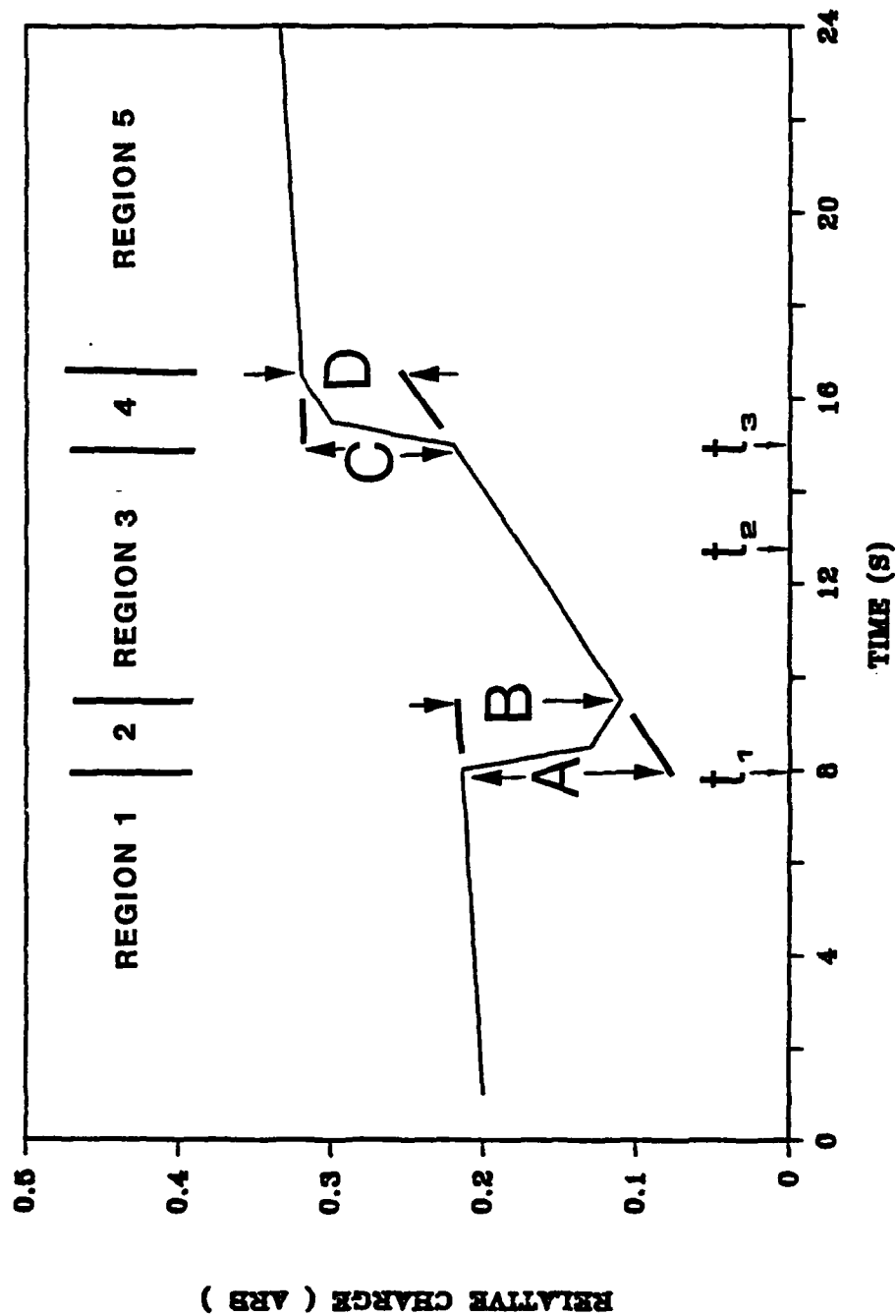
FIG. 4. Relative charge versus time for "dunk" displacement change measurements. The various estimates, A, B, C, and D, of the displacement change are defined.
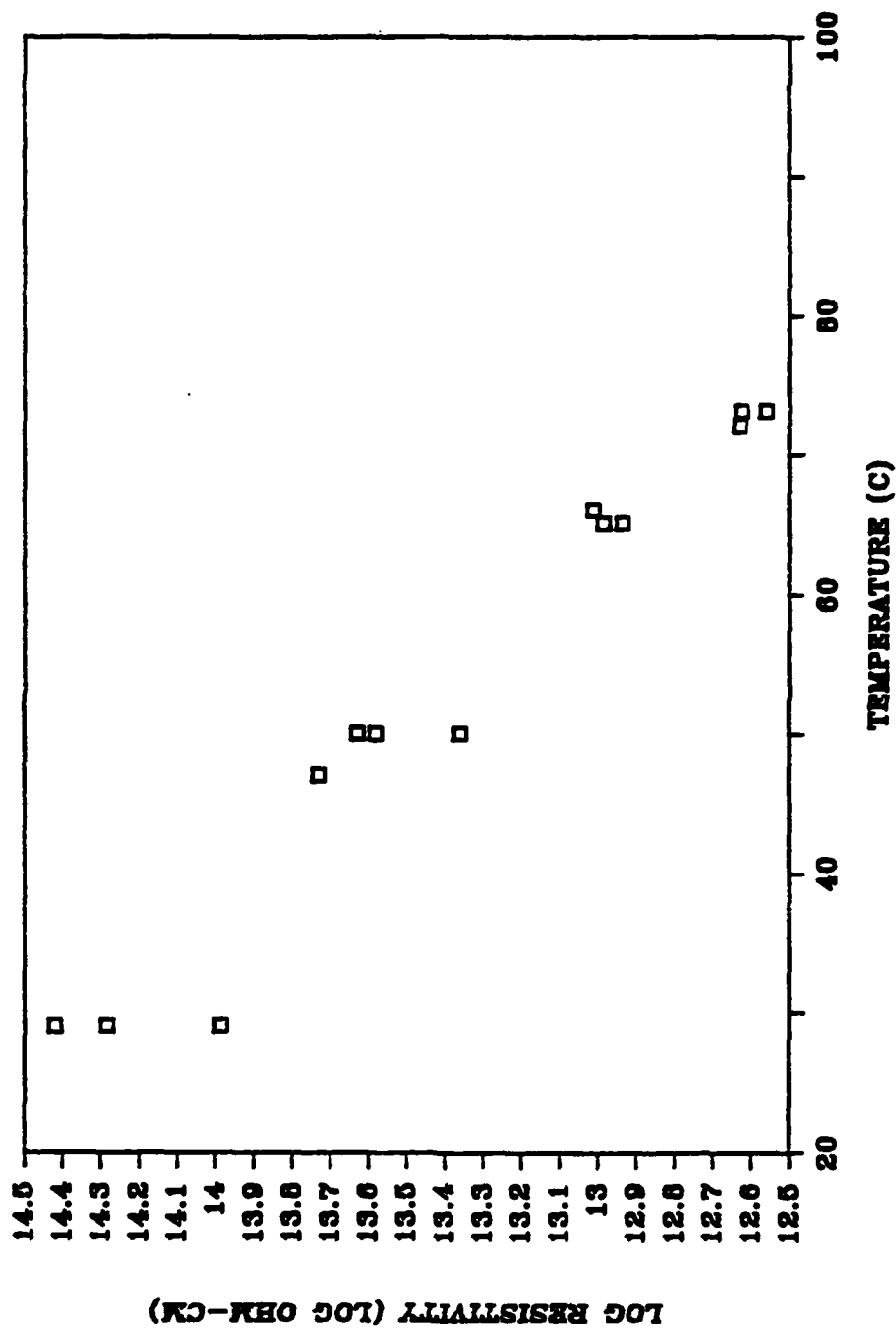
FIG. 3. Logarithm of resistivity versus temperature for 52/48 P(VDF-TrFE).
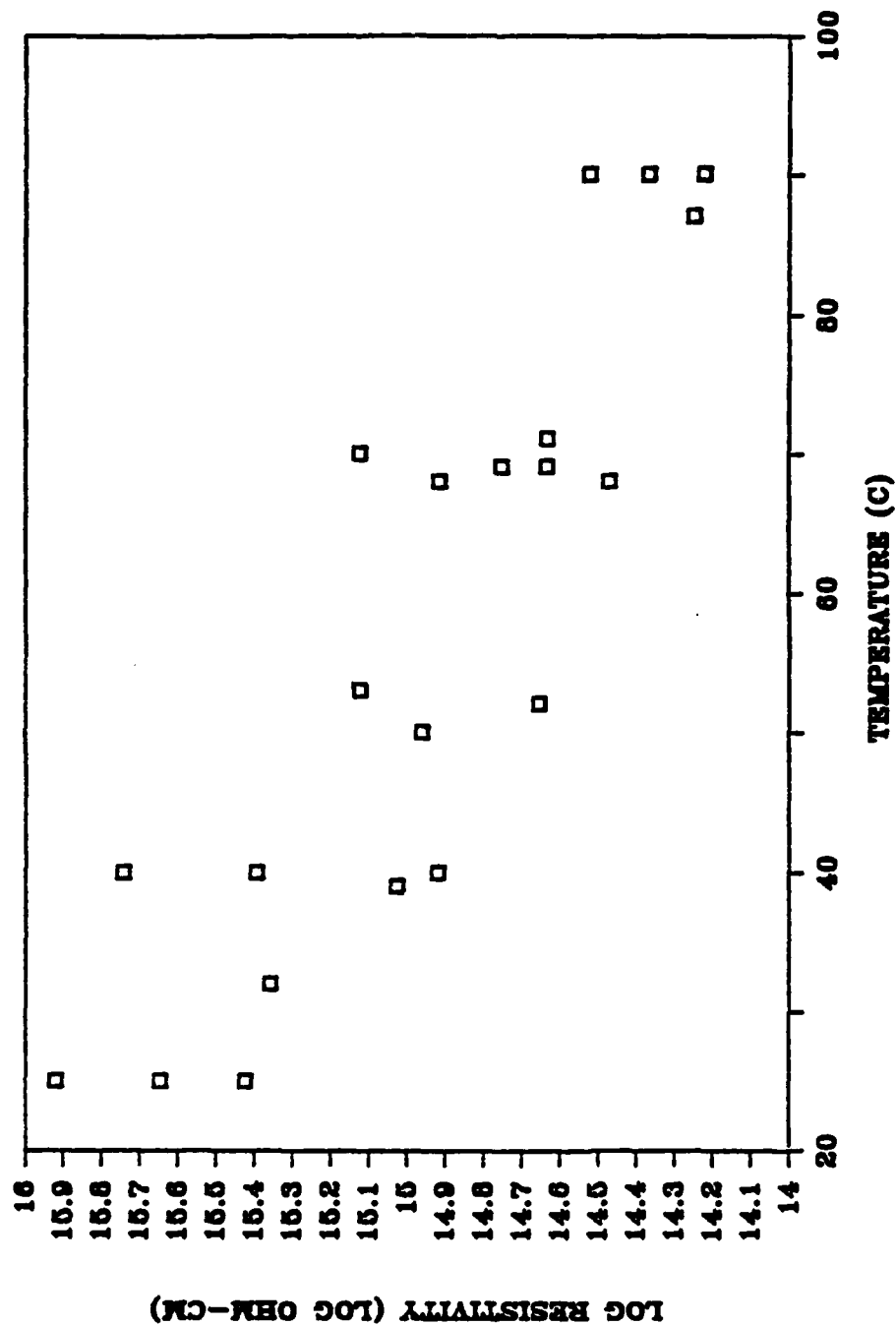
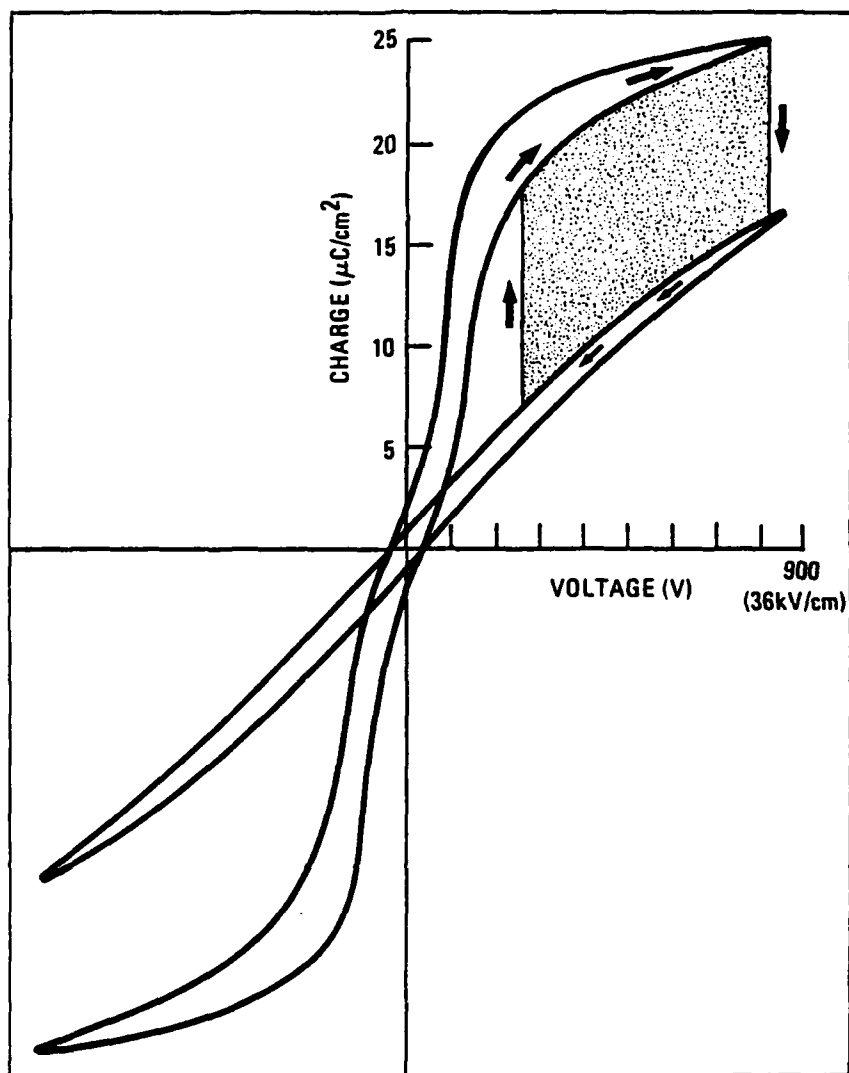FIG. 2.   Logarithm of resistivity versus temperature for 73/27 P(VDF-TrFE).

FIG. 1.   Electrical energy production cycle may be realized by
appropriately phased changes in temperature and applied
electric field. The shaded area is equal to the
electrical energy per cycle which may be produced by
0.025-cm-thick
$Pb_{0.99}Nb_{0.02}(Zr_{0.68},Sn_{0.25},Ti_{0.07})_{0.98}O_3$.
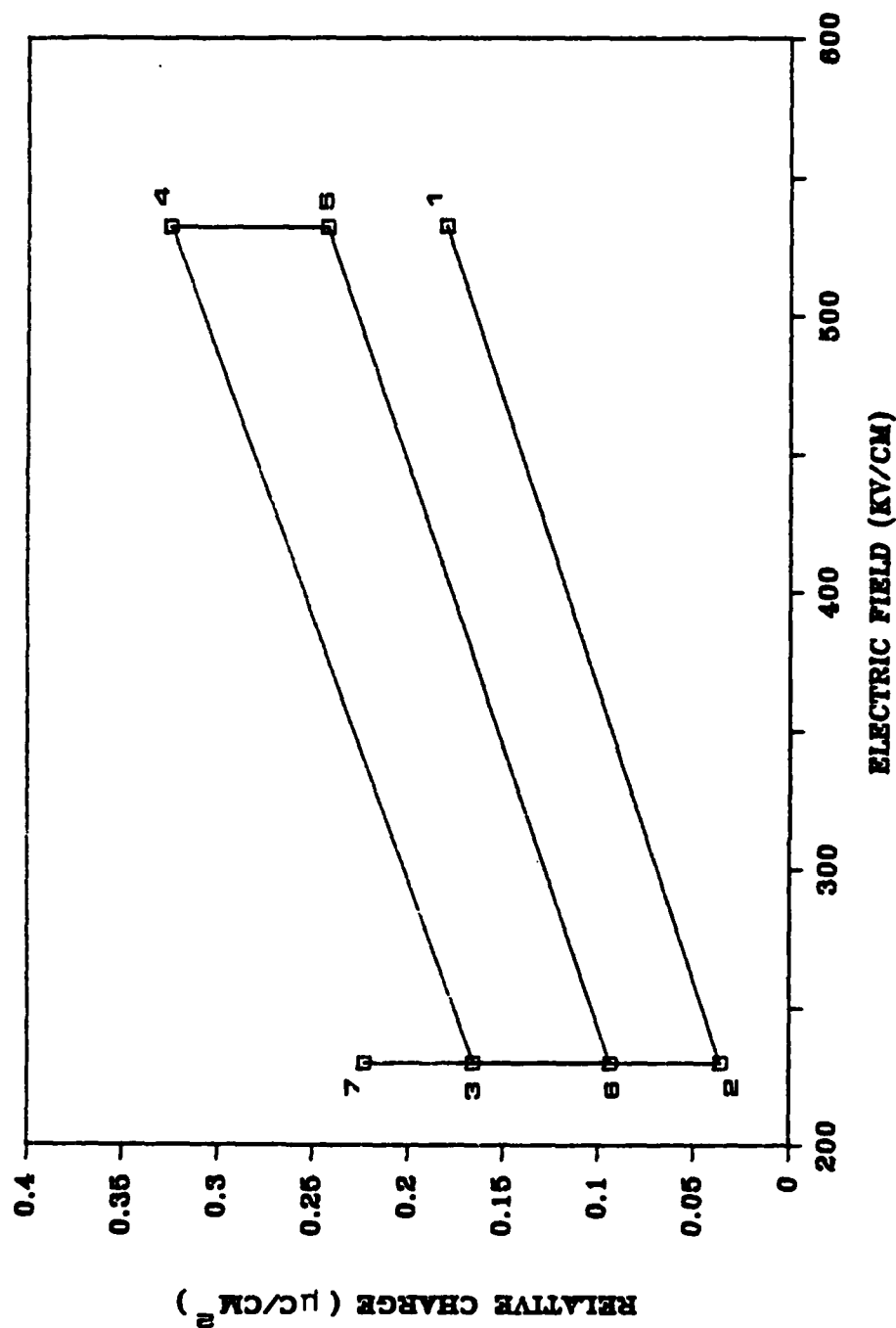The taller loop corresponds to 146C and the other
loop was recorded at 171C.

FIG. 15. A modest pyroelectric conversion cycle. The cycle suffers from drift due to conduction of charge through the bulk of the specimen. The copolymer is 73% VDF. The temperature limits of the 12.6 second period cycle are 23C and 67C.

49

END

FILMED

11-85

DTIC